

# A Classical Picture of the Role of Vacancies and Interstitials in Helium-4

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Received: 4 March 2008 / Accepted: 3 July 2008 / Published online: 23 July 2008  
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**Abstract** Motivated by experimental hints for supersolidity in Helium-4, we perform Monte Carlo simulations of vacancies and interstitials in a classical two-and three-dimensional Lennard-Jones solid. We confirm a strong binding energy of vacancies which is of the order of the Lennard-Jones attraction. This is reminiscent of what has been found for vacancies in Quantum Monte Carlo simulations. In addition, we find a strong attraction and large binding energy of interstitials in two-dimensional simulations. This is mainly due to the formation of a pair of dislocations by clustering interstitials, which minimizes the elastic deformation energy. We interpret the results in light of the properties of Helium-4.

**Keywords** Helium · Lennard Jones · Vacancies · Interstitials · Phase separation · Monte Carlo · Binding

## 1 Introduction

A supersolid is a conjectured phase of matter which possesses the seemingly contradicting properties of having spatial long-range crystalline (positional and orientational) order as well as being superfluid at the same time. Potential evidence for such a supersolid phase in Helium-4 has first been detected as a nonclassical moment of rotational inertia (NCRI) in torsional oscillator experiments by Kim and Chan

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(KC) in 2004 [1, 2], more than thirty years after the first proposals by Andreev and Lifshitz [3] and Chester [4]. Based on the idea of a supersolid phase in a bosonic quantum crystal with vacancies (or interstitials), a number of theoretical explanations have been proposed [5–8].

Although NCRI for Helium-4 has also been observed by other experimental groups [9–11], it remains controversial whether this is a supersolid phase or if the interpreted supersolid phase is a bulk equilibrium phenomenon [9–13]. Computer simulations have shown that the density matrix of Helium-4 crystal decays exponentially [14, 15] and vacancies in solid Helium-4 are gapped [16]. Non-equilibrium vacancies present in solid Helium-4 attract each other and phase separate, thus the Helium crystal purges itself of vacancies [16]. This shows that the ground state of a single crystal Helium-4 is not a supersolid [17]. It is remarkable that the solid with the strongest quantum properties known in nature behaves so classically.

Therefore, the understanding of the effective vacancy-vacancy interaction and interstitial-interstitial interaction is crucial to our understanding of this phenomenon. Here we set to carry out a classical Monte Carlo simulation in order to compare with the properties of Helium-4. We find that a classical modeling of Helium yields vacancy and interstitial binding energies that are larger than in the quantum case. However, the phase remains essentially the same, showing that the attraction of vacancies and interstitials in Helium-4 can be understood at a classical level.

In Sect. 2 we introduce the methodology used to study the physics of vacancies (Sect. 3) and interstitials (Sect. 4), which are the main focus of this work. The conclusions are presented in Sect. 5.

## 2 Simulating a Classical Lennard-Jones Crystal

For our classical Monte Carlo simulations we model the interaction between two atoms by a Lennard-Jones potential, where we fix units by choosing parameters suitable for Helium-4 [18]:

$$\phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (1)$$

with  $\sigma = 2.56 \text{ \AA}$  and  $\epsilon/k_B = 10.2 \text{ K}$ .

We perform classical Monte Carlo simulation in the NPT ensemble of constant particle number, pressure, and temperature using two types of moves. The first type is a local particle displacement: we propose to move a randomly chosen particle by a random distance in the interval  $[0, \sigma)$  for the simulation of vacancies in a crystal, and by a random distance in the interval  $[0, \sigma/4)$  for the simulation of a crystal with interstitials. The second type is a volume change, where we propose to vary the volume of the system by adjusting the length, width and height of the system individually within a range of  $\pm 2.5\%$ .

Initially, we start from a perfect triangular lattice for our two-dimensional (2D) or from a perfect hexagonally closed packed (hcp) lattice for our three-dimensional (3D) simulations. For a solid with vacancies, we randomly remove particles from the

system, while for a solid with interstitials, we randomly add particles to the system. In our simulations, we define one sweep as  $1000N^2$  trial particle moves (where  $N$  is the number of particles in the system), followed by one volume-changing move in each dimension.

We probe for attractive interactions and binding of vacancies and interstitials by calculating the binding energies and inverse compressibility. The inverse compressibility can be measured as

$$\kappa^{-1} = \frac{\partial^2 G}{\partial N^2}, \quad (2)$$

where  $N$  is the number of particles in the system and  $G$  is the Gibbs energy [19] given by

$$G = \sum_{i < j} \phi(|\vec{r}_i - \vec{r}_j|) + pV - k_B T N \ln V. \quad (3)$$

While quantum mechanically Helium-4 forms a crystal only at a pressure above 25.46 bar, classically a crystal is already formed at zero pressure. Therefore, we use a pressure of only  $P = 1$  bar in our constant-pressure classical Monte Carlo simulations.

Thermodynamically, phase separation will occur when  $\kappa^{-1} < 0$ . Numerically, the inverse compressibility is computed as

$$\kappa^{-1} = G(N+1) + G(N-1) - 2G(N). \quad (4)$$

The binding energy of a system with  $p$  vacancies can be expressed as

$$E_B(N_0, p) = G(N_0 - p) + (p-1)G(N_0) - pG(N_0 - 1), \quad (5)$$

and that of  $p$  interstitials as

$$E_B(N_0, p) = G(N_0 + p) + (p-1)G(N_0) - pG(N_0 + 1), \quad (6)$$

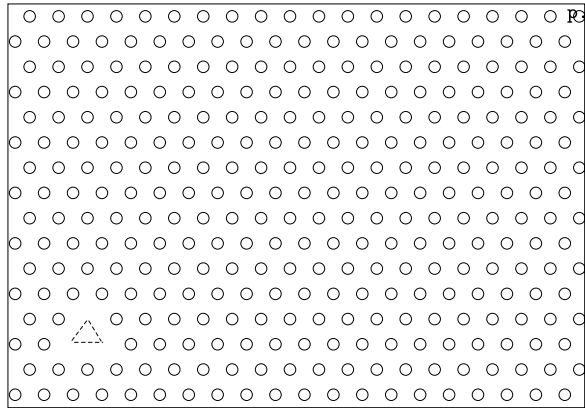
where  $N_0$  is the number of particles of the commensurate crystal.

### 3 Vacancies in a Classical Crystal

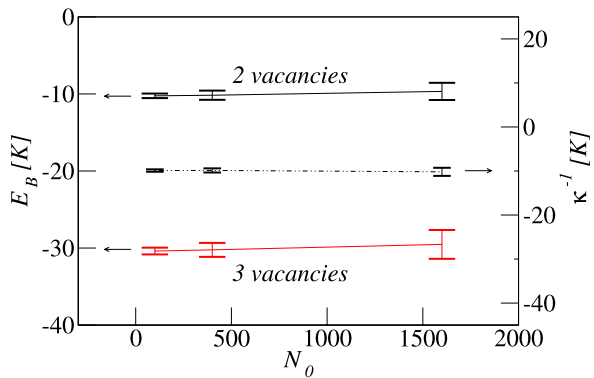
For the simulation of vacancies we consider systems with 1, 2 and 3 vacancies respectively. To find the ground state, we perform a numerical annealing process. Due to the simple structure of energy space of vacancy systems, a rapid annealing schedule can be used. We start from a temperature of 1 K and reduce it by a factor of 2 every 100 sweeps until we reach a final temperature of 0.01 K.

As shown in Fig. 1, vacancies have a tendency to bind and form a vacancy-cluster. The three-vacancy cluster shown to be the ground state of the classical system is also the most likely configuration in the Quantum Monte Carlo simulations of Ref. [16]. In classical systems the interparticle distance is given by the position where the potential reaches its minimum; this is why we see no distortion of the crystal in Fig. 1 (in contrast to the quantum case of Ref. [16]).

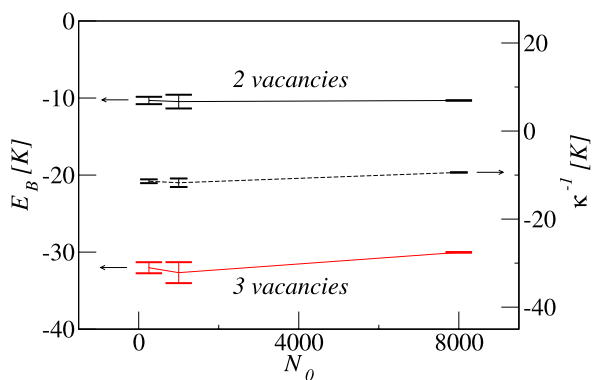
**Fig. 1** Snapshot of a typical configuration showing a stable vacancy cluster. There are  $N_0 = 400$  lattice positions and three vacancies, the temperature is  $T = 0.01$  K, pressure  $P = 1$  bar, and density  $n = 0.139 \text{ \AA}^{-2}$ . Periodic boundary conditions are used



**Fig. 2** (Color online) Binding energy  $E_B$  and inverse compressibility  $\kappa^{-1}$  of two and three vacancies in two dimensions at  $T = 0.01$  K,  $P = 1$  bar as a function of the number of particles  $N_0$  in a commensurate solid. The arrows point to the corresponding axes of the data

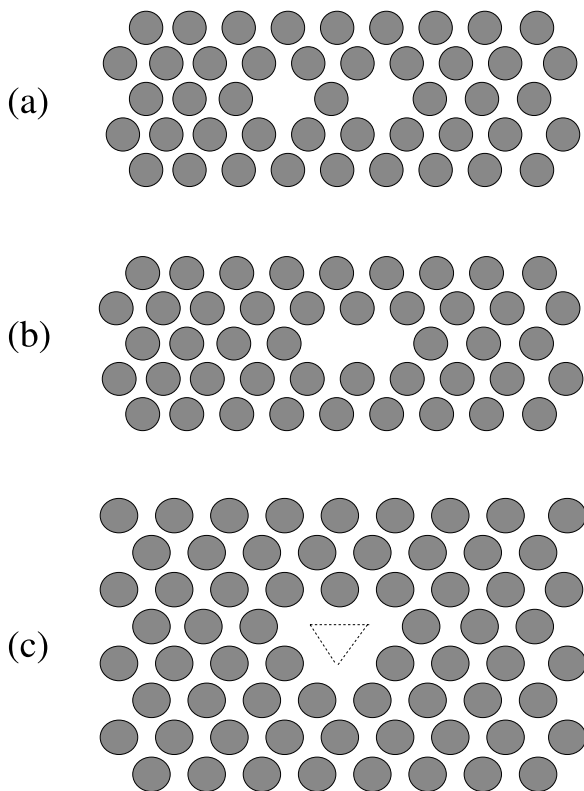


**Fig. 3** (Color online) Binding energy  $E_B$  and inverse compressibility  $\kappa^{-1}$  of two and three vacancies in three dimensions at  $T = 0.01$  K,  $P = 1$  bar as a function of the number of particles  $N_0$  in a commensurate solid



In Figs. 2 and 3, we show the two-vacancy binding energy, the three-vacancy binding energy, as well as the two-vacancy inverse compressibility at a temperature  $T = 0.01$  K and pressure  $P = 1$  bar for two and three dimensions.

**Fig. 4** The binding of vacancies: **(a)** shows the configuration before and **(b)** after the formation of a two-vacancy cluster. By binding vacancies the number of nearest neighbor atoms is increased by one and the bound state is stabilized. **(c)** The three vacancies form three pairs, indicated by the *three dashed lines*. As a result, a three-vacancy cluster is expected to have a binding energy three times that of a two-vacancy cluster



From the Lennard-Jones potential, the classical minimum interaction energy between two Helium atoms at zero temperature and zero pressure is exactly  $\epsilon = -10.2$  K. (This is slightly higher at finite pressure or temperature.) Comparing Figs. 4(a) and (b), we find that if two vacancies cluster, the system will be stabilized by the energy of one pair of atoms, which costs about  $-10$  K at finite temperature and pressure. This argument shows that our simulation results for the binding energy of two vacancies in Figs. 2 and 3 are sensible.

For a three-vacancy cluster (Fig. 4(c)) there are three pairs of interaction and the binding energy is therefore approximately three times as much as that of a two-vacancy cluster. Therefore, the value of  $-30$  K is once again expected. The clustering of vacancies can also be understood from minimizing the surface energy of a vacancy cluster. The surface in contact with the crystal is much lower for a vacancy cluster than for individual vacancies.

Similar effects have been seen in quantum Monte Carlo (QMC) simulations, where a binding energy of around one Kelvin for two vacancies and of several Kelvin for three vacancies in three dimensions has been observed [16, 20]. The substantial reduction of the binding energy is mainly due to quantum zero point effect. Although these values are much reduced, they are still sufficient to cause phase separation of vacancies [16]. Qualitatively, the classical picture applies also to the quantum Helium-4 system.

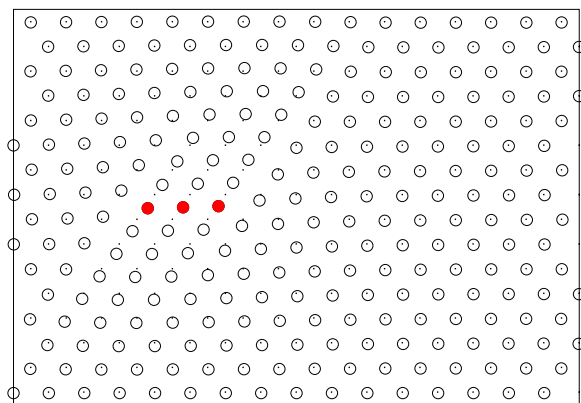
## 4 Interstitials in a Classical Crystal

Unlike the case of vacancies, where it is relatively easy to locate the global minimum, the interstitial system possesses many meta-stable local minima. To search for the ground state, we have to perform a stimulated tempering simulation. Instead of using the much more involved conventional parallel tempering approach [21–24], we use a simpler method that works well in our interstitial case.

The updates were identical to the case of vacancies, except that one row of atoms was fixed to prevent the crystal from rotating. Otherwise, the interstitials will be removed when the system chooses a different orientation by rotating. From an initial temperature of 0.1 K the temperature is decreased in an annealing procedure, taking care that the energy does not drop by more than 0.2 K in 100 sweeps. Repeated simulations (starting from different initial conditions) have been carried out. More than 80% of these simulations yield the same lowest energy configuration, which we can safely call the global minimum. Our results again show the binding of interstitials. A typical configuration is shown in Fig. 5.

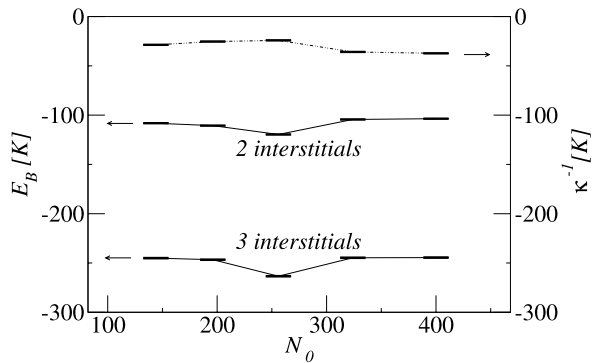
We observe that at low temperatures the interstitials will be individually inserted into neighboring rows, creating a pair of dislocations, connected by a line of extra particles (see Fig. 5).

The binding energy and inverse compressibility are shown in Fig. 6. Surprisingly, we find even larger binding energies for interstitials than for vacancies. Interstitials cost more energy because they significantly distort the crystal, and much of this extra energy can be recovered by the binding of interstitials into a line connecting two dislocations as seen in Fig. 5.



**Fig. 5** (Color online) A typical configuration with  $N_0 = 256$  atoms and three extra interstitials,  $T = 10^{-7}$  K,  $P = 1$  bar,  $n = 0.141 \text{ \AA}^{-2}$ . *Open circles* represent the position of the atoms; *dots* represent an imaginary perfect lattice and *solid circles* represent the interstitials. To select the interstitials, we first superpose the actual configuration onto a virtual perfect commensurate lattice. Consequently, we match each lattice point with the closest actual particle in the configuration. Finally, we remove all these matches and the remainder of the atoms are considered as interstitials. The final aspect ratio of the configuration is 0.889 (cf. 0.867 of a NVT configuration), showing that simulations with a fixed aspect ratio will fail in finding the lowest energy configuration

**Fig. 6** Binding energy  $E_B$  and inverse compressibility  $\kappa^{-1}$  of two and three interstitials in two dimensions as a function of the number of particles  $N_0$  in a commensurate solid at  $T = 10^{-7}$  K,  $P = 1$  bar



## 5 Conclusions

Our classical Monte Carlo simulations of vacancies and interstitials in a classical solid show strong attraction and binding of vacancies and interstitials in a Lennard-Jones crystal. This is highly detrimental to the formation of a supersolid in the quantum mechanical case, where vacancies and interstitials are delocalized. Similar full quantum simulations of vacancies in Helium-4 show that while the binding is strongly reduced by quantum fluctuations, it is still large enough to cause vacancies to be expelled from the crystal instead of forming a supersolid. Although the behavior of interstitials in solid Helium has not been studied in detail yet (apart from a lattice modeling [25]), it is established that they cost a finite energy gap  $\Delta = (22.8 \pm 0.7)$  K [16] to create. The strong binding seen in the classical case combined with the larger effective mass for interstitials indicates that the strong attraction will remain in the quantum case.

**Acknowledgements** The ALPS libraries [26, 27] were used for parallelization and error evaluation. The simulations were performed on the Hreidar cluster of ETH Zürich and the hpcpower cluster of HKU. We acknowledge fruitful discussions with J. Wang, G.H. Chen, S.Q. Shen, and P. Corboz. Financial support from RGC of HKSAR is also greatly acknowledged.

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